

DEPARTMENT OF COMMERCE

Bureau of Standards

Certificate of Analyses

OF

STANDARD SAMPLE No. 90

FERROPHOSPHORUS

ANALYST	PHOSPHORUS
H. A. Bright, Bureau of Standards	26.19 ^a 26.21 ^b
Booth, Garrett & Blair, Philadelphia, Pa.	26.15 ^a 26.14 ^c
P. R. Hurd and W. C. Bowden, jr., Ledoux & Co., New York, N. Y.	26.15 ^a
A. B. Gerber, Southern Manganese Corporation, Anniston, Ala.	26.02 ^a
John L. Harvey, Carnegie Steel Co., Duquesne, Pa.	26.08 ^d
C. E. Nesbitt, Carnegie Steel Co., Braddock, Pa.	26.29 ^e
R. J. Price, Electro Metallurgical Co., New York, N. Y.	26.2 ^f
Messrs. Fry and Furey, Electro Metallurgical Co., Niagara Falls, N. Y.	26.2 ^a
Average	26.16
Recommended value	26.2

^a Fused with Na_2O_2 ; precipitated with molybdate and then twice with MgCl_2 .

^b Dissolved in H_2SO_4 (specific gravity, 1.84) and then as in (^a).

^c Fused with Na_2O_2 , and then precipitated and weighed as ammonium phosphomolybdate.

^d Dissolved in H_2SO_4 (specific gravity, 1.84) and then precipitated twice with MgCl_2 in the presence of citric acid.

^e Dissolved in HClO_4 and then as in (^a).

^f Same results obtained by (^a) and by solution in HNO_3 -HF and then as in (^a).

George K. Burgess

Director.

Washington, D. C.
(October 1, 1928)

SUGGESTED METHOD FOR UMPIRE DETERMINATION OF PHOSPHORUS IN FERROPHOSPHORUS

In this method the sample is fused with Na_2O_2 in an iron crucible, the melt dissolved in HNO_3 , the phosphorus separated as ammonium phosphomolybdate and precipitated twice with MgCl_2 .

Solutions required.—**MOLYBDATE SOLUTION.**—Mix 100 g of pure MoO_3 or 118 g of 85 per cent molybdic acid with 400 ml of water and add 80 ml of NH_4OH (sp. gr. 0.90). When solution is complete, filter and pour the solution slowly and with constant stirring into a mixture of 400 ml of HNO_3 (sp. gr. 1.42) and 600 ml of water. Let settle for 24 hours and use the clear supernatant liquid.

AMMONIUM NITRATE SOLUTION (5 PER CENT).—Dissolve 50 g of NH_4NO_3 in 950 ml of water.

AMMONIUM HYDROXIDE.—**AMMONIUM CITRATE SOLUTION.**—Dissolve 25 g of citric acid in 350 ml of water and add 200 ml of NH_4OH (sp. gr. 0.90).

DILUTE AMMONIUM HYDROXIDE (1 : 20).—Mix 50 ml of NH_4OH (sp. gr. 0.90) and 1,000 ml of water.

DILUTE HYDROCHLORIC ACID (1 : 20).—Mix 50 ml of HCl (sp. gr. 1.19) and 1,000 ml of water.

MAGNESIA MIXTURE.—Dissolve 50 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 100 g of NH_4Cl in 500 ml of water. Add NH_4OH in slight excess, let stand overnight, and filter if a precipitate appears. Make barely acid with HCl and dilute to 1,000 ml.

PROCEDURE.—Mix 1.5 g of the finely powdered alloy (150 mesh or finer) with approximately 15 g of dry Na_2O_2 in a 40 ml Armco iron (low phosphorus) crucible stamped from No. 20 gauge metal. (These crucibles can be purchased from The Consolidated Metal Products Co., Dayton, Ohio.) Spread a thin layer of Na_2O_2 over the top of the mixture, cover the crucible with a porcelain or iron lid, and fuse the contents of the crucible by heating first at a low temperature and then gradually raising the temperature until complete fluidity of the mass occurs. When the charge has melted rotate the crucible sufficiently to take care of unattacked particles of the alloy along the sides of the crucible and also to stir up the melt. Keep the contents of the crucible molten for about five minutes, then heat to bright redness for a minute, remove from the heat source and allow to cool.

Place the crucible in an 800 ml covered beaker containing about 300 ml of water, warm for a few minutes, remove the crucible and wash it well with a warm 1 per cent solution of HNO_3 . Neutralize the solution by slowly adding HNO_3 (sp. gr. 1.42) and then add 40 ml in excess. Digest until the solution clears—a little iron scale will usually remain in-

soluble. Filter the solution through a tight paper into a certified 500 ml volumetric flask and wash the residue with the warm 1 per cent solution of HNO_3 . Cool to 20°C ., dilute to exactly 500 ml, mix well, and pipette duplicate 100 ml portions (0.3000 g) into 600 ml beakers.

Add 20 ml of HNO_3 (sp. gr. 1.42), 5 to 10 ml of a 1.5 per cent solution of KMnO_4 , and carefully boil until manganese is precipitated. Dissolve the precipitate by the addition of H_2SO_3 and boil for a few minutes to expel oxides of nitrogen. Cool somewhat, add 40 ml of NH_4OH (sp. gr. 0.96) and 160 ml of filtered ammonium molybdate solution. Digest at 50°C . for one to two hours with frequent stirring. Cool to room temperature and filter on a paper of close texture, keeping as much of the precipitate as possible in the beaker. Wash the beaker and the precipitate five times with a 5 per cent solution of NH_4NO_3 . Set the filtrate and washings aside after thorough mixing and make sure that no further separation of phosphomolybdate occurs.

Dissolve the precipitate in the beaker in 25 ml of ammonium hydroxide-ammonium citrate solution. Pour this solution through the filter which contains the remainder of the yellow precipitate and catch the solution in a 400 ml beaker. Wash the beaker and paper several times with a dilute solution of NH_4OH (1 : 20), next with a little hot water, then with hot dilute HCl (1 : 20) and finally with dilute NH_4OH (1 : 20). The volume of the solution at this point should be approximately 150 ml. Neutralize the ammoniacal solution with HCl , using litmus as indicator, and add 1 ml of HCl (sp. gr. 1.19) in excess and 20 ml of magnesia mixture per decigram of phosphorus. Now add NH_4OH (sp. gr. 0.90) dropwise and with continuous stirring until the solution is ammoniacal and most of the phosphorus has been precipitated. Finally add 15 ml more of NH_4OH and allow the solution to stand for four hours or overnight at room temperature. The time of standing may be reduced to two hours if the solution is kept in a refrigerator or an ice-water bath and is frequently well stirred. Filter wash the magnesium-ammonium phosphate precipitate several times with dilute NH_4OH (1 : 20), and dissolve it on the filter in 25 ml of dilute HCl (1 : 1), catching the solution in the original beaker containing the bulk of the precipitate. Wash the filter thoroughly with dilute HCl (1 : 20) (note 1) and dilute the solution to 150 ml. Cool to 10°C ., add 0.2 g of citric acid, next 2 to 3 ml of magnesia mixture, then, while

stirring well, add NH_4OH (sp. gr. 0.90) dropwise until the precipitate dissolves slowly and with difficulty. Continue the neutralization by adding dilute NH_4OH (1 : 20) dropwise and with stirring until precipitation appears complete. Finally add sufficient NH_4OH (sp. gr. 0.90) to provide an excess of 3 to 5 per cent by volume. Allow to stand as before. Transfer the precipitate to a 9 cm Whatman No. 42

filter or its equivalent and wash with dilute NH_4OH (1 : 20). Ignite the precipitate carefully and at as low a temperature as possible until the carbon has been destroyed. Finally ignite to constant weight at a temperature of 1,000 to 1,050° C., and calculate to phosphorus by multiplying the weight of $\text{Mg}_2\text{P}_2\text{O}_7$ by 0.2787 (note 2). Correct the final result by blanks carried through all of the steps of the method.

NOTES

1. If the alloy contains significant amounts of arsenic (over 0.1 per cent), treat the HCl solution with H_2S , digest, filter, and wash with acidulated hydrogen sulphide water. Boil the filtrate to expel H_2S , add 0.2 to 0.3 g of citric acid, 2 to 3 ml of MgCl_2 mixture, etc. Small amounts of arsenic can be removed by adding 1 g of NH_4Br and carefully boiling the HCl solution to a volume of 10 ml.

2. The ignited and weighed $\text{Mg}_2\text{P}_2\text{O}_7$ may, if desired, be examined for SiO_2 , by dissolving in dilute HCl , adding 5 ml of H_2SO_4 (sp. gr. 1.84), fuming, diluting, filtering off the insoluble which can be ignited, weighed, and treated in the usual manner with HF and H_2SO_4 for silica.

3. Instead of fusing a 1.5 g sample, individual 0.3 g samples may be fused with 4 to 5 g of Na_2O_2 , in which case the HNO_3 solution should be concentrated to about 100 ml before precipitating with molybdate.

4. Tests made at this bureau show that the Bureau's standard ferrophosphorus No. 90 can be dissolved in concentrated sulphuric acid without loss of phosphorus. This can be conveniently done by transferring a 0.3 g sample to a small, dry, covered beaker or Erlenmeyer flask (100 to

150 ml), adding 6 ml of sulphuric acid (sp. gr. 1.84), and heating at 150 to 160° C. until decomposition is complete and no black particles remain. Solution is usually complete in 60 to 90 minutes.

5. Tests on the precipitation of 0.0659 g of phosphorous (≈ 0.2365 g $\text{Mg}_2\text{P}_2\text{O}_7$) by an excess of magnesia mixture in the presence of 0.2400 g of iron and 5 g of citric acid showed that all but a few tenths of a milligram of phosphorus is precipitated. The procedure used was as follows: To the acid solution, having a volume of about 150 ml and containing 5 g of citric acid, add 25 ml of magnesia mixture, cool to 10° C., gradually neutralize with NH_4OH and then add 25 ml in excess. Stir the solution for 15 to 20 minutes, digest at room temperature for several hours or preferably overnight. Filter, dissolve, and reprecipitate under standard conditions. It is always necessary to reprecipitate the magnesium ammonium phosphate under standard conditions in order to secure a precipitate ultimately corresponding on ignition to $\text{Mg}_2\text{P}_2\text{O}_7$ —cf. The analysis of phosphate rock, G. E. F. Lundell and J. I. Hoffman, *Jl. Assoc. of Official Agri. Chemists* 8, No. 2, p. 184.